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ANALYSIS BY FLAMELESS ATOMIC ABSORPTION

FINAL REPORT

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See following executive summary

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Executive Summary

We have found that the wire loop can be successfully used as an electro-thermal atomizer for flameless atomic absorption spectroscopy and is competitive with carbon rod and carbon cup atomizers. The wire loop is slightly less sensitive than carbon atomizers but is much simpler and cheaper to operate. Although for some samples the wire loop is not as prone to matrix effects as carbon atomizers, these effects must be considered. The method of standard additions was shown to be successful in reducing or eliminating matrix problems.

Wire loop methods for zinc, iron, silver, chromium, manganese, barium, lead, copper, cadmium, selenium and arsenic were developed and optimized. The use of a sheathing gas, hydrogen mixed with argon or nitrogen, during the heating cycle was found to improve the sensitivity of this technique. The brief signal obtained with the wire loop required electronic modification (reduction of the capacitance of the damping capacitors) of the Varian AA5 Atomic Absorption Spectrophotometer to provide the faster instrument response required. Detection limits on the order of a few parts per billion are possible with the wire loop technique.

Sensitivity and reproducibility for more volatile elements such as As and Se can be improved by use of a glass absorption cell (with quartz windows) to keep the atoms in the light path. Attempts to distinguish between the signals from Cr(III) and Cr(VI) were not successful; however, an extraction method for Cr(VI) was successfully employed to separate it from Cr(III) prior to analysis. Methods were also developed for using the wire loop in analysis of a variety of organic samples.

The wire loop method was tested against EPA standard water samples and Army natural water samples. The Army samples were natural waters that had been previously analyzed by other atomic absorption methods. Data from these tests indicate that the wire loop methods have a standard deviation of less than 5% and an accuracy acceptable for water quality analysis.

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I. Introduction

With the first successful non-flame atomizer constructed from graphite by L'Vov[1] in 1961, the capability to determine sub-ppm or part per billion (ppb) concentrations and picogram quantities of metals became a reality. These non-flame atomizers are heated electrically and may or may not have a flame associated with them. Many non-flame atomizers have been recorded in the literature. The L'Vov Furnace consisted of a 30 to 50mm long, 2.5 to 55mm i.d. graphite tube heated electrically by an a.c. current to temperatures up to $2500^{\circ}C$. To prevent the atomic vapor from permeating the porous graphite walls of the tube, they were lined with Ta or W foil, or with a thin layer of pyrolytic graphite.[2] The sample was introduced by placing it on a graphite electrode which was then fitted into the graphite tube and heated to atomize the sample.

Massmann[3] described an improved graphite-tube atomizer for atomic absorption spectroscopy in which the sample was introduced through a small hole in the center of the tube (55mm long, 6.5mm i.d) by means of a micropipet. The tube could be heated by means of a 500A power supply to $2600^{\circ}C$ in several seconds.

The basic L'Vov graphite-tube furnace, later modified by Massmann, was further modified by the Perkin-Elmer Corporation and sold commerically. The most recent development of the commercially available graphite atomizer is the opposed-flow gas system in which the gases flow from the ends to the center of the tube, and the vapor exiting through the sample introduction port, thereby reducing atomic vapor condensation. Furthermore, the purge gas flow may be interrupted, which also decreases the transport of the atomic vapor out of the graphite tube.[4]

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Woodriff[5-8] et al described another version of a graphite-tube atomizer, which could be heated to temperatures up to 3000°C. Sample introduction was either by fine spray nebulization or through a small graphite cup inserted into a side arm. Robinson et al[9] described a graphite heated tube for the direct determination of metals in air. As air passed through a bed of graphite, metals reacted with heated graphite and were reduced to metal atoms. The atomic vapor then passed through a quartz absorption tube positioned in the light path. An induction heated graphite-tube furnace was described by Langmyhr and Thomassen.[10]

A different type of graphite atomizer, known as the West filament atomizer[11] consisted of a 20 mm long,2 mm i.d,graphite filament placed between stainless steel electrodes and heated by an electrical current to 2,500°C in about 5 sec. in an argon atmosphere. Sample aliquots of 1 to 5 μℓ were placed on the filament for analysis. An improved West-type filament, described by Alder and West[12] used different inert gas flows and introduced a masking guide to prevent filament emissions from entering the monochromator entrance slit during analysis.

A commercially available atomizer by Varian-Techtron,based principally on the West-type filament and Massmann carbon rod atomizers,consists of two graphite electrodes supporting either a tube or cup with a pyrolytic graphite surface. The 9 mm long, 3 mm i.d. tube requires 1 to 5 μℓ samples. The cup may accept up to 20 μℓ samples. Hydrogen and either nitrogen or argon gases are admitted through a diffusing screen.

Another type of carbon atomizer of the filament variety was reported by Montaser and Crouch,[13,14] known today as the graphite braid atomizer. This atomizer needed less power for operation and therefore required no water for cooling as did the other atomizers.

The graphite atomizers mentioned above, generally exhibit the following advantages over flame atomizers:

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(1) They are much more efficient than a flame at converting the sample to the atomic vapor form.

(2) The atomic vapor is contained in a much smaller volume, thus effectively concentrating the sample.

(3) Better sensitivity and low background and audible noise are obtained.

(4) Although matrix matching between sample and standards is sometimes required, solvents do not in general affect the atomic absorption, since the solvents evaporate prior to vaporization of the sample.

(5) There are no explosion hazards

(6) Solid sample analysis is possible.

There are also some disadvantages with graphite atomizers:

(1) They are more expensive than flame atomizers.

(2) Their electrical power consumption is on the order of 1 kw, require water cooling, and a 30-60 sec. waiting between analyses.

(3) Interferences are generally more common and more severe than with flame atomizers.

(4) The relative precision is about 3 to 8% compared to about 1% for flame atomizers.[2]

(5) The atomization is accomplished in a very short time requiring fast response detector systems to suitably follow the signal.

Attempts to reduce power consumption and reduce or omit water cooling have resulted in metallic filament atomizers. Donega and Burgess[15] developed electrically heated tantalum and tungsten boats requiring no water cooling and reduced amounts of power. Temperatures of $2,200^{\circ}C$ could be attained in less than 0.1 sec. Hwang et al[16-18] modified the Donega and Burgess system by using a tantalum ribbon rather than a boat, and this was previously offered by Instrumentation Laboratory, Inc. as the model 355 Flameless Sampler. Other

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tantalum atomizers have been developed by Takeuchi[19] et al, Maruta and Takeuchi,[20] and Sensmeier, Wagner and Christian.[21]

Cantle and West[22] developed a tungsten filament using 1-$\mu\ell$ samples. This atomizer, when compared with the carbon filament types, required much less voltage to reach the same temperature. Wire loops made of copper,[23-25] silver,[26] gold[27] and platinum[28] have been successfully employed for the analysis of mercury. Usually the mercury is collected on the wire by electrolysis. The high temperatures required for most other metals would melt these wires. An electrically heated tungsten coil atomizer was developed by Williams and Piepmeier.[29] The filament taken from a commercial light bulb, was heated in the center of a vertical quartz tube protected by a flow of argon. A tungsten rhenium alloy has been used with direct aliquot sampling,[30,31] preconcentration of metals,[32] and indirect methods of analysis[33] in the laboratory.

Recently there have been several types of sources employed in atomic absorption spectroscopic analysis. Variations of hollow cathodes include multielement,[34] demountable,[35] high intensity,[36] and pulsed mode lamps.[37-39] Electrodeless discharge[40,41] lamps have also been widely accepted as an intense source, especially for elements whose resonance lines lie in the ultraviolet region below 200 nm. Other sources employed in atomic absorption include lasers[42,43] and continuum[44] sources. An excellent review of sources of atomic spectroscopy is given by Goldstein and Walters.[45,46]

Photomultiplier tubes predominate as the detectors for atomic absorption spectrophotomers. Yet other detectors have been used. Among them are interferometers,[47] vidicon tubes,[48,49] photodiode arrays,[50] resonance detectors[51,52] and photoionization detectors.[53]

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The applications of atomic absorption, and related techniques range far and wide in chemical analysis. Lundgren and co-workers employed a photodiode (radiation programming) to accurately control the temperature of a heated graphite tube within $\pm$ 10°C and applied the system to the analysis of metals in biological tissue[54] and cadmium in blood[55] and seawater.[56] Other applications of the carbon tube have been the determination of trace metals in water,[57-59] zinc in sea-bottom sediments,[60] cadmium in biological matrices[61] and lead in blood.[62,63] Various versions of the graphite furnace, developed by Perkin-Elmer Corporation, have found application in saline[64] and freshwater[65-67] analyses, and in the determination of cadmium in biological materials,[68] in copper in edible oils,[69] and zinc.[70]

Graphite filaments were extensively characterized for atomic absorption spectroscopy (AAS) and atomic fluorescence spectrometry (AFS) by T. S. West and coworkers,[71-73] and applied to the analysis of numerous elements in a variety of matrices. Among these were the determination of cadmium, gold, and manganese in lubrication oils,[83,84] nickel in crude and residual oils,[85] and lead in "instant" coffee and tea powders.[86]

The carbon rod atomizer has been applied to the anlaysis of biological[87] and clinical samples by AAS and AFS,[88] including the determination of copper[89] and iron[90] in blood serum, and gold, cobalt, and lithium in blood plasma.[91] Winefordner's as well as Chakrabarti's groups employed the carbon rod for analyzing wear metals in engine oils,[92,93] lead in petroleum and petroleum products,[94,95] vanadium in crude oils,[96] silver and copper in jet engine oil by AFS,[97] and a variety of metals in lubricating and crude oils.[98,99] Silver and copper may be determined sequentially by taking advantage of their different volatilities.[100] Silver and gold have also been analyzed in geological and metallurgical samples using the carbon rod.[101] Fairless and Bard employed

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electrodeposition on graphite rods for the analysis of copper.[102] The importance of rapid detection systems for transient signals was pointed out by Maessen and Posma for the carbon rod atomizer.[103]

The tantalum filament has been applied to the analysis of barium and antimony in gunshot residues,[104] lead in blood,[105] lead, silver, and indium in rainwater,[106] trace metals in water, chromium in steel,[107] and for the introduction of analyte into plasmas.[108] The tantalum boat was used for the determination of zinc in seawater.[109]

Bratzel et al used both platinum and tungsten wire loop atomizers for atomic fluorescence spectrometric studies.[110] Crouch's group has also evaluated platinum wire loops for use in AAS and AFS.[111] A platinum-rhodium alloy has been developed by the National Bureau of Standards for the determination of lead in paint using flame techniques.[112] Cresser and Mullins[113] calculated the temperature-time curves for tungsten and graphite filaments and concluded that current filament designs are open to much improvement.

Electrodeposition on platinum and tungsten wires[114] has been used for the analysis of cadmium in urine[115] and seawater by AAS. Mercury, cadmium, lead, and nickel deposited electrochemically on silver wire electrodes, were analyzed by exploding the wire electrode and subsequently measuring the atomic emission.[116] The Zeeman effect has been employed in atomic absorption measurements as a means of background detection.[117]

A rather new application which appears to open up a new area of atomic absorption spectroscopy, is the use of this technique as a chromatography detector. In this manner metal speciation, (i.e. the chemical form of the metal) is determined. Recently atomic absorption detection has been employed for chromatography,[18] liquid chromatography, and high performance liquid

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chromatography.[119] For further information, the interested reader is directed
to a review given by Fernandez.[120]

Previously in our laboratory, Davis and co-workers have developed tungsten-
rhenium wire loops constructed from a 97% tungsten-3% rhenium alloy, as electro-
thermal atomizers. The loops have been employed with some success.[55-58]

The purpose of this study was to develop a reproducible non-flame atomizer
with improved sensitivity, precision and accuracy. Refinements of the previously
published survey work were found necessary to make such improvements. Refine-
ments included a closer investigation into the effects of gas flows, optical
alignment, geometry and solution conditions. Specifically, zinc, iron,
manganese, barium, selenium, tin, lead, cadmium, copper, silver, chromium and
arsenic have been investigated. These metals are of environmental concern, as
they are all either essential to the human diet or toxic to the human body.
The effects of interferences upon the analytes' signal has been investigated
and compared to similar effects with a commercially available atomizer. A
number of improvements have been accomplished in the application of the wire
loop atomizer to the analysis of metals in natural waters and in samples of
biological interest.[121] Digestion procedures have been established employing
a microwave oven technique. Furthermore, important alterations in the atomizer
head design and construction material have allowed for significant improvement
in optical alignment.[121] A new atomizer design permits direct analysis of
relatively volatile elements such as selenium. This atomizer is more con-
venient and rapid than chemical vaporization techniques and offers comparable
sensitivities. Atomization temperatures can be reproduced leading to improved
reproducibility. It has been demonstrated that our electronic detection system
is not ideal for reliably reproducing the atomization process with the wire
loop atomizer. Some improvements in the detector response have been accomplished.

To further characterize the wire loop atomizer, studies of the mechanism of atom formation have been made and the results compared with the results of similar studies with graphite atomizers.

II. Experimental

A. Glassware.

Doubly-distilled, deionized water was produced by distillation of distilled water with a Corning Mega-Pure one liter still followed by passage through a Corning LD-3 General Purpose Demineralizer equipped with Corning 3508-B high capacity disposable demineralizer cartridges. The specific resistance of the water was greater than 2×10^6 ohms/cm which is defined by the Environmental Protection Agency as ultrapure water.[122]

All glassware, linear polyethylene and polypropylene containers were soaked in either 50% nitric acid or 1:1 conc. nitric acid/sulfuric acid for at least three days before thorough rinsing with tap water to eliminate all traces of acids followed by several rinses with doubly-distilled, deionized water.[121] Five-and ten-ml disposable beakers, supplied by Calbiochem, Hicksville, New York, were employed for most work. Polypropylene beakers supplied by Bollab, Inc., Derry, N.H., were also employed.

B. Apparatus

Unless otherwise specified, a Varian-Techtron Single Beam AA-5 Spectrophotometer was employed. Depending on the width of the mechanical entrance slit (25 to 300 microns) the Ebert grating monochromator provides a spectral resolution of 0.3Å to 9.9Å. Varian-Techtron hollow cathode lamps modulated at 285 Hz were used throughout this work. In general, the Varian-Techtron AA5 Spectrophotometer was set up according to the manufacturer's suggested lamp currents. The burner head was removed from the commercial atomizer base and replaced with the wire loop atomizer. A five $\mu\ell$ sample aliquot was dispensed onto the wire loop. Either with the modified Varian-Techtron CRA63 power

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supply or the homemade power supply low voltage was applied to the loop to atomize the sample. During the analysis period nitrogen or argon and hydrogen were passed over the loop at various flow rates, as described in the results, and were monitored by Gilmont Flow meters. The normal sampling technique was to place 5 $\mu\ell$ of sample solution on the wire with a Varian "Autopette" fitted with disposable pipet tips. The sample was dried and atomized from the wire loop into the optical path of the spectrometer as discussed below. The detector was an HTV type R-446 photomultiplier tube. The amplification system basically consisted of linear and logarithmic amplifiers together with a phase sensitive detector tuned to 285Hz, in order to discriminate against spurious background radiation. Signals were recorded with a Varian-Techtron A25-Single pen recorder with a full scale response of 0.5 seconds. Scale expansion controls were calibrated up to 10X on the atomic absorption unit.

Consistent curvature was observed with all elemental calibration curves, as can be seen in Figure 1. It is quite possible to atomize a sample in less than 0.1 seconds and the authors believe that increased linearity would be obtained with improved designs of this atomizer, but electronics appears to be a major part of the problem.

Several approaches could have been taken to obtain evidence that the electronics was the problem. A new detection system could have been bought or built, or amplifiers in the system could have been changed. A simpler modification to the system, recommended by Varian,[123] solved the problem. Changes in capacitors in the circuitry were made to reduce the RC time constant. Specifically, capacitors labelled C12 and C14 in #5-02, P.M. amplifier, of the Varian-Techtron AA-5 Instrument Manual (Oct., 1971) were replaced with 0.01 μF capacitors. As one will observe in Figures 2 and 3, an improvement in both

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Figure 1

Calibration Plots for Mn and Fe
Before Amplifier Modification
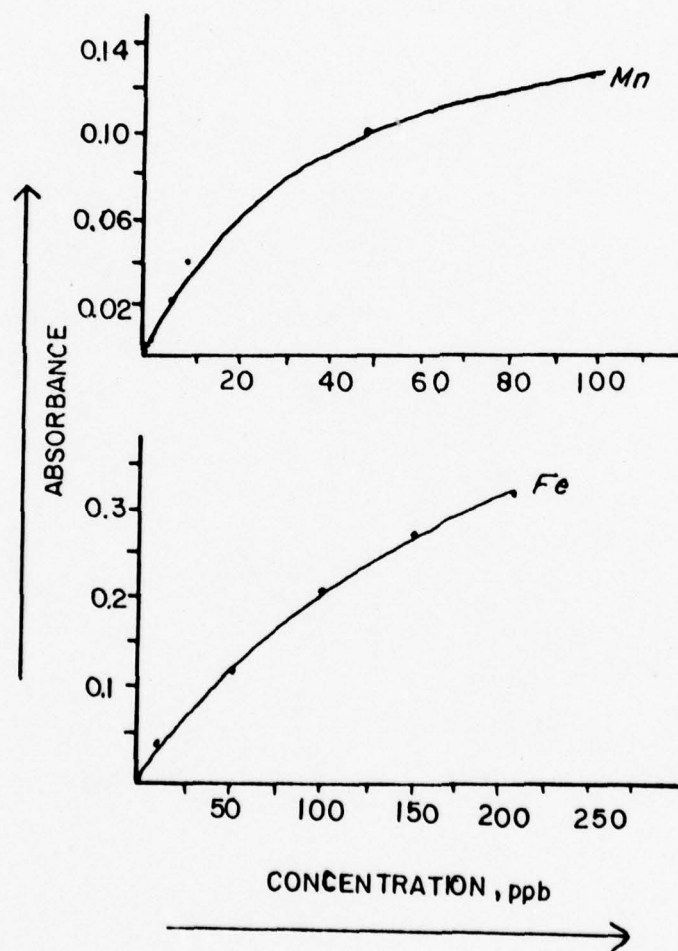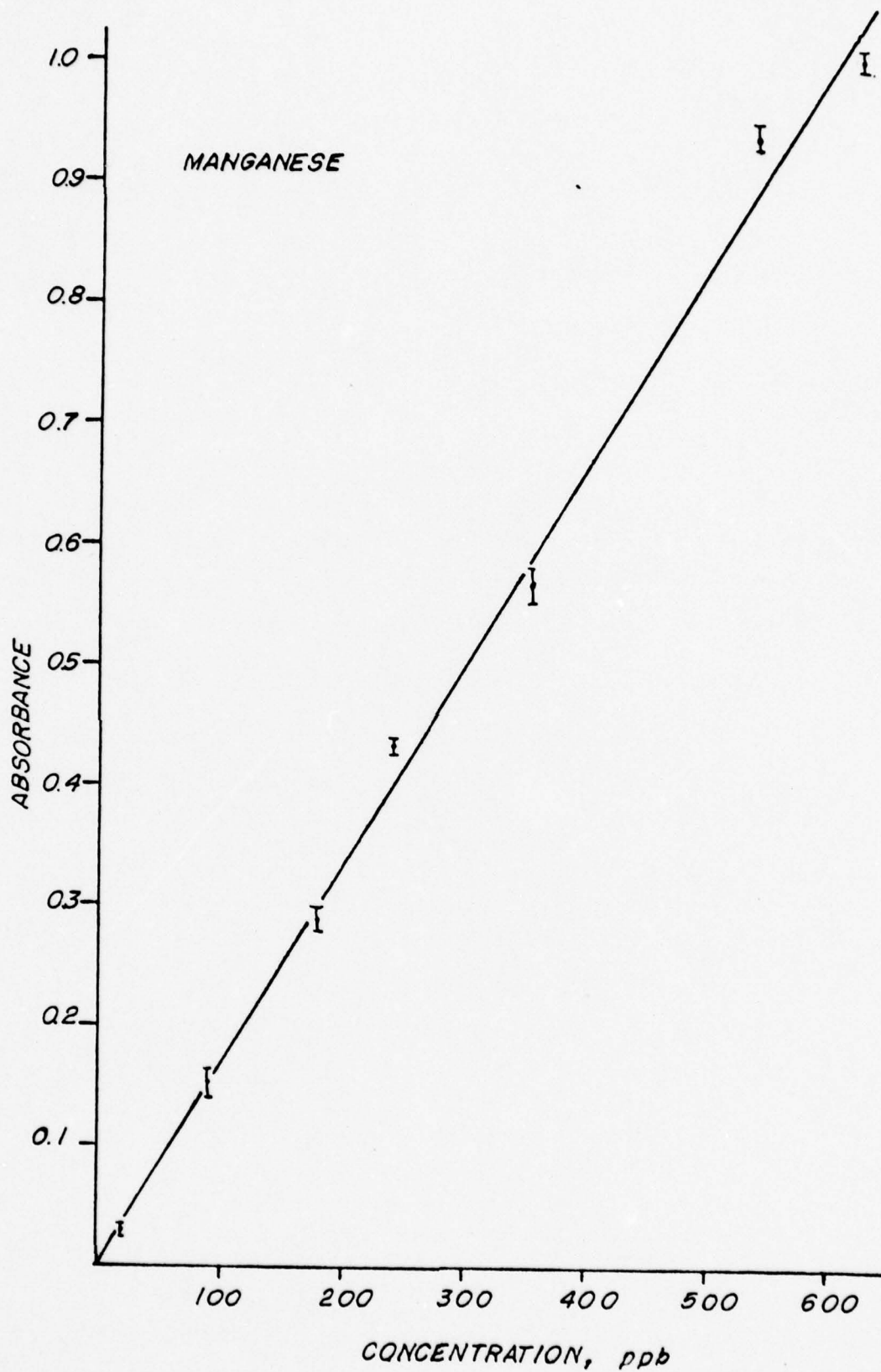
Figure 2

Calibration Plot for Manganese after Amplifier Modification

Figure 3

Calibration Plot for Iron

Iron after Amplifier Modification
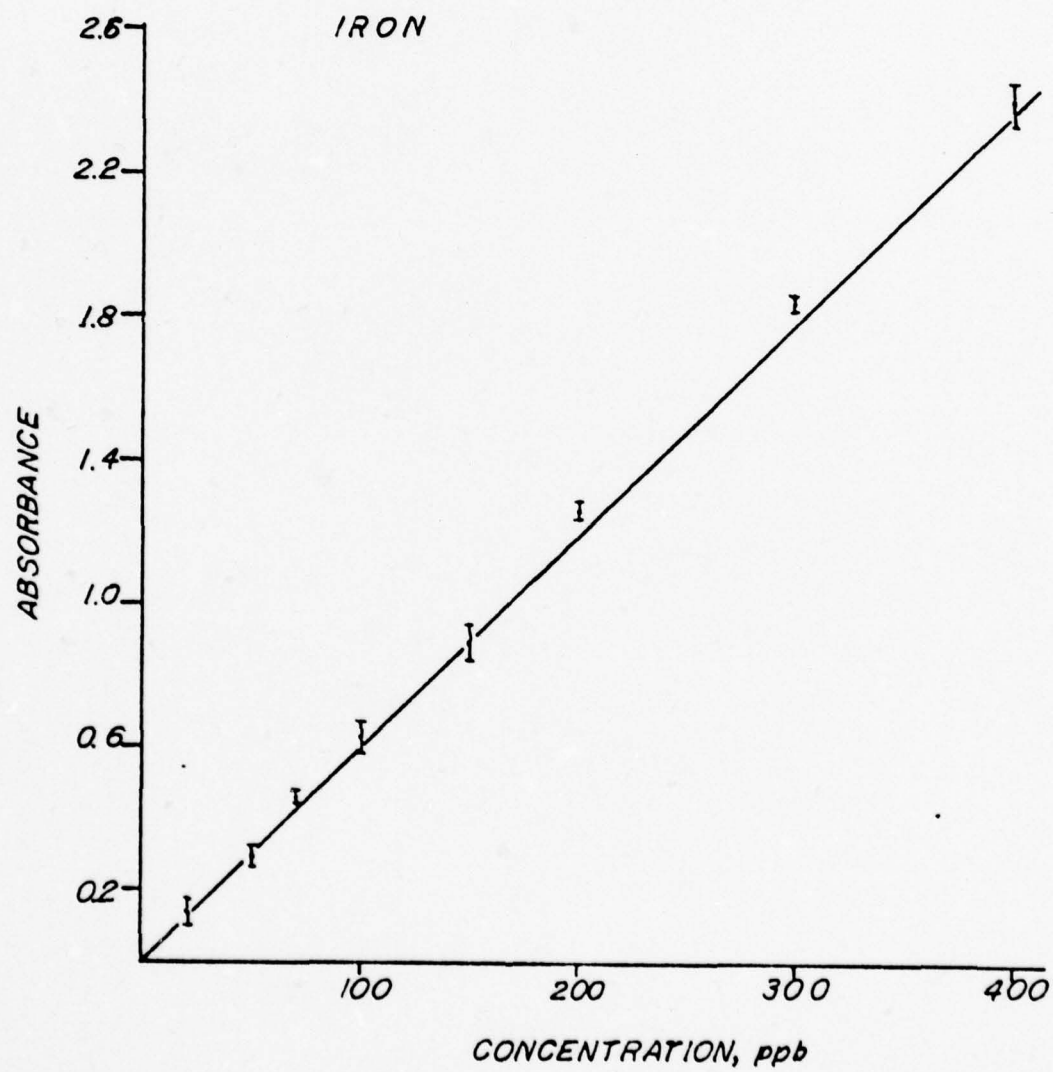
sensitivity (slope of the calibration curve) and range of linearity were obtained. Indeed, this indicates that, at least in part, the detection system was responsible for the non-linearity exhibited in Figure 1.

It should be pointed out a Perkin-Elmer instrument model (306) fitted with a baffle specifically designed for carbon furnaces gave much better results than the Varian AA-5 using the wire-loop atomizer. A test run on such an instrument showed a linear relation between absorbance and concentration at least to 125 ppb of Mn and the absorbance at 125 ppb was 0.85 as opposed to the wire loop value of 0.20 (Fig. 2). This indicates that the P-E instrument is probably capable of better sensitivities than the Varian instrument. This is somewhat expected since the Perkin-Elmer graphite furnace is both longer and larger in diameter than the Varian CRA-63 and would allow for longer atom residence times.

It has previously been determined by Maessen and Posma[103] that formation and shape of the absorption signals by carbon rod analysis are influenced by the time constant of the amplifier-detector-recorder system. A time constant of 0.3 seconds was measured for the Varian-Techtron AA5 atomic absorption spectrophotometer. The full scale response time for the recorder employed was measured by using a square wave generator. A full scale response of 0.27 seconds was obtained. Therefore the recorder could respond to all atomization signals and was not a contributing factor in the non-linearity of the calibration plots.

Contrary to the heating characteristics of graphite atomizers, the wire loop atomizer heats to its final temperature almost instantly. It would be expected that atomization would occur at the same rate. By use of an oscilloscope, measurements of absorbance-time profiles were recorded. The

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absorbance was measured at the output of the logarithmic amplifier rather than the output of the detector. This probably reduced the time constant inherent in the circuitry. The absorbance peak (full scale) was obtained in less than 0.3 seconds and in fact, usually in less than 0.2 seconds. From this information, it is quite conceivable that the detection system was causing non-linearity.

A means of background correction (non-atomic absorption) was provided by use of a Varian-Techtron model BC-6 Simultaneous Background Corrector. In this system the total absorption and background absorption are continuously measured. By means of a 'Polka Dot' mirror, the hollow cathode lamp and the hydrogen continuum lamp are aligned along the optical path and are identically focused on the entrance slit of the monochromator. The signals from the two lamps are electronically separated by the BC-6 system and background correction is applied electronically. The BC-6 system corrects for background absorption up to 1.0A at all wavelengths between 193.7 nm and 357.9 nm.

A Varian-Techtron Carbon Rod Atomizer (CRA) Model 63 together with a CRA-63 Power Supply was employed in this work as a referee method of analysis. The referee method of analysis provides a way to compare the analytical results obtained by the wire loop atomizer for samples of unknown concentrations.

Several variations of an electrothermal wire loop atomizer designed in this laboratory and constructed in the machine shop at the University of New Orleans were employed in this work. The best results were obtained with base atomizers machined from grade C phenolic blocks. For the Varian AA5 these were mounted on the burner base and gases introduced into the burner bases. For Perkin-Elmer instruments the base was of brass with attachments for gas tubes on the side. Two enclosures were used. For most elements the enclosure was of brass (Fig. 4), but for very volatile elements (Se and As) a long glass enclosure with quartz windows was used to contain the vapors in the light

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path for a longer time (Fig. 5).

At first, a homemade power supply was employed with the wire loop atomizer. A 12-volt stepdown transformer (Stancor, P 6378) in combination with a variable transformer (Variac) supplied the current necessary to heat a wire loop. Three Variacs were employed; one "drying" Variac was set between 0 to 14% in the 120% full scale mode of the original supplied voltage; the "stepped atomize" Variac was set between 20% and 45% in the 140% full scale mode of the original supplied voltage; or in place of the stepped atomize Variac, a Variac driven by a motor was employed to allow for a linear voltage program (LP). A variable voltage supplied to the motor allowed for different linear voltage programs.

For adaptation of the CRA 63 Power Supply to the wire loop atomizer a modification described by Cooper and Dunckley[124] was made, which allowed for an interruption of the analytical cycle. Also an adjustable rheostat (Central Scientific Co., 12.3 amperes, 2.8 ohms) was placed in series with the power supply to provide for the correct range of voltage to operate the wire loop atomizer.

The wire loop consisted of a 97% tungsten - 3% rhenium alloy (General Electric 3D 218-CS Process). A template designed and constructed in this laboratory was employed to provide for a reproducible wire loop geometry.

For the elements investigated the atomization temperatures were determined using a Leeds and Northrup 8632C optical pyrometer. A single adjustment potentiometer type was employed for temperature measurements during the atomization process. To monitor the established temperatures, an IR photocell similar to that of Woodriff[125] was constructed and calibrated with the optical pyrometer. The photocell was mounted on the optical rail at a distance of 2 cm from the entrance slit of the monochromotor.

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Figure 4

Wire Loop Atomizer with

Standard Brass Enclosure

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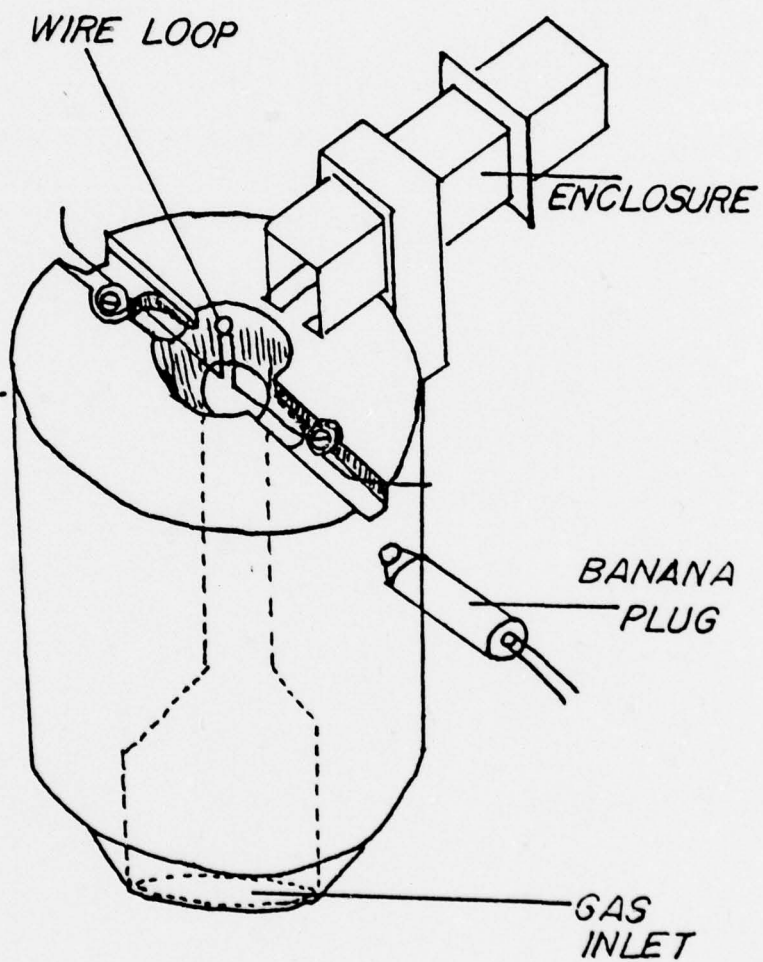
Figure 5

Wire Loop Atomizer with Glass Absorption
Cell (Quartz Windows) for Volatile Elements

ABSORPTION CELL

WIRE LOOP

BANANA PLUG

GAS INLET
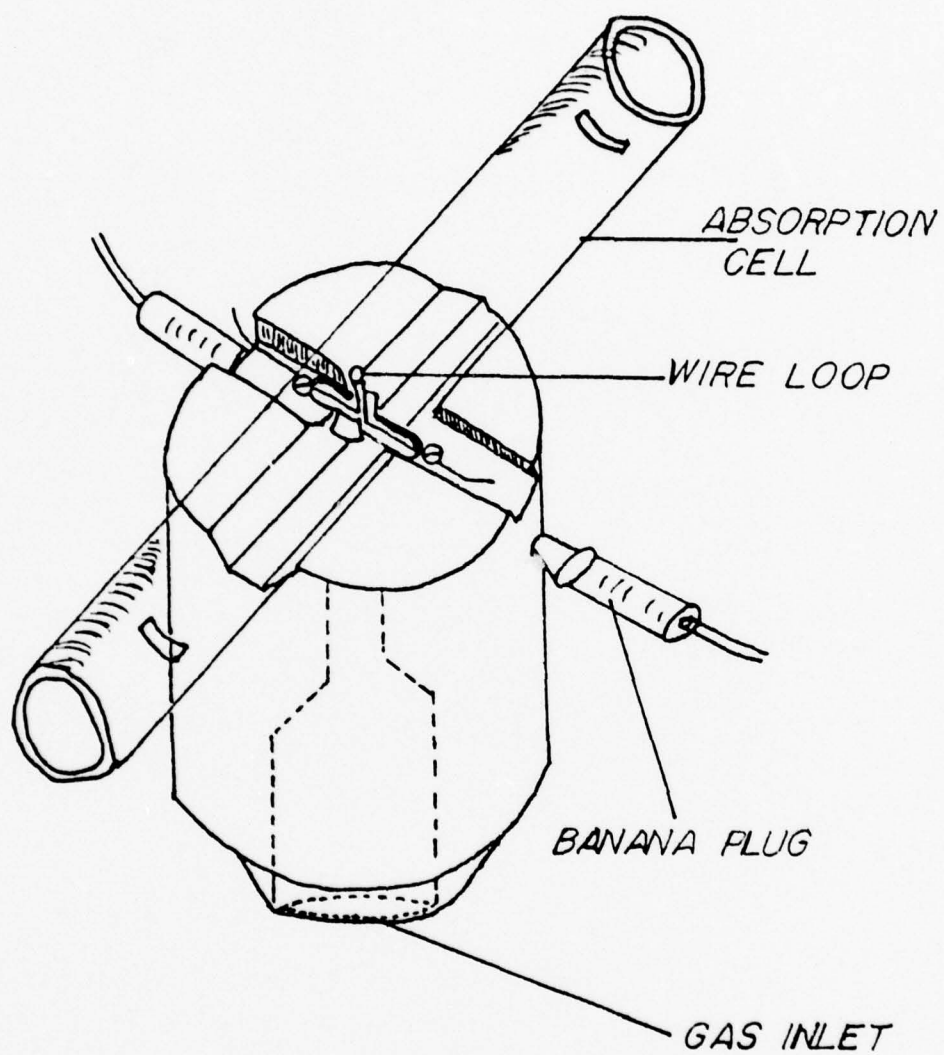
C. Drying and Atomization Temperatures

The temperatures of atomization were monitored by a photocell. The output of a photovoltaic cell was fed to a variable gain operational amplifier. The output of the amplifier was fed to a meter and strip chart recorder. The gain control was adjusted to provide a suitable reading for the temperature range of interest. A calibration curve was obtained with the CRA63 power supply in its modified configuration since this system was used most often. Table 1 lists the temperatures associated with the stepped and ramped atomization modes. In the stepped mode, applied voltages, and thus temperatures, are changed "instantaneously from one selected value to another while in ramped mode the voltages are changed continuously with time from a lower value to a higher one. With this calibration, all temperatures for optimum and appearance signals were obtained. Table 2 contains similar information relating Variac settings which were used in the earliest portion of this work.

A small hole was drilled in the center of the photocell which was then placed in a 2-cm long cylindrical enclosure. This grey-black enclosure reduced the amount of stray radiation impinging on the photocell. This design allowed the continuous monitoring of the temperature while simultaneously obtaining the sample signal via the hole in the photocell. The placement of the hole in the cell was not critical. The temperature could be monitored to assure that the wire loop maintained its integrity. In later work it was found that mounting the photocell next to the opening of the enclosure was a better approach since drilling a hole in the photocell cracked its surface.

This photocell responds to the infrared emissions from the hot tungsten-rhenium wire. Temperatures below $700^{\circ}C$ could not be measured with this type of silicon photodiode. Tungsten emissions at temperatures between 200 and

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Table 1

CRA63 Power Supply Settings and Related Temperatures

CRA63 Instrumental Settings	Temperature ^{o}C	
	Step	Ramp
3.0	----	1125
3.5	----	1280
4.0	710	1455
4.5	820	1550
5.0	935	1630
5.5	1040	1680
6.0	1150	1730
6.5	1260	1740
7.0	1370	1745
7.5	1470	1800
8.0	1570	1830
8.5	1650	1845
9.0	1725	1855
9.5	1795	1858
10.0	1860	1860

Ramp rate setting of 5.5

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Table 2

Variac Setting vs Temperature

Variac Dial Setting, % of Total	Temperature, ^{o}C	
	100% = 140 volts setting	100% = 120 volts setting
20	860	860
25	1030	1150
30	1470	1360
35	1540	1525
40	1740	1650
45	1850	----

$500^{o}C$ are in the far infrared region of the spectrum and are quite weak. However, the calibration plot is sufficiently linear that drying temperatures below $700^{o}C$ could be determined by extrapolation.

The most suitable temperatures for evaporation of the solvent were between 100 and $300^{o}C$. It was important not to evaporate the solvent too quickly, since rapid boiling would cause splattering of the sample off the wire and large errors would be obtained. If the sample is heated to a high temperature there is some loss of the analyte due to its vaporization. Drying times varied between 40 sec and 60 sec, depending on the volatility of the element. The more volatile the element, the lower the temperature and the longer the time necessary to remove the solvent during the drying stage.

The atomization temperature is a critical parameter. A typical relationship between atomization temperature and absorbance is shown at the optimum gas flow rates for barium, in Table 3 At low temperatures, the sample is atomized slowly and a broadened signal is observed, while at very high temperatures the atomization occurs so quickly that the detector cannot follow the signal. All elements show similar curves but the curve for barium shows a narrower optimum temperature range than most.

For a portion of this work the homemade power supply was used. The general method of analysis, when using this power supply, included a low applied voltage to dry the solvent and a higher applied voltage to atomize the sample. The atomizer Variac was then raised beyond the optimum atomization setting to clean the wire and readjusted to the optimum setting.

Experience demonstrated that in most cases it was not necessary to clean the wire after each analysis. Little or no observable residue remained on the wire after most analyses and interferences which would occur because of an unclean wire were not observed. When residual material was left on the wire, a linear voltage programming atomization was preferred. The temperature

Table 3

Dependence of Absorbance on Variac Setting

Variac Setting	Absorbance (for Ba)
25	0.006
30	0.16
35	0.40
40	0.60
42	0.66
43	0.68
45	0.64
50	0.31

could be set beyond the atomization temperature and the ramp rate could be set to give the optimum signal. Furthermore, this mode of atomization could in many instances alleviate many of the background interferences.

Except for optical alignment, the absorption cell atomizer is affected by the parameters discussed above in the same manner as the brass enclosure wire loop atomizer (Figures 4 and 5). Maximum absorbance values were obtained when the top half of the wire was in the optical path. Also the temperatures for atomization of selenium and arsenic are not as critical as with the other elements when the brass enclosure atomizer is used.

D. Digestion of Biological Materials

A microwave oven (General Electric Model JET 84 with output wattages of 580 watts and 360 watts on high and low settings, respectively) was employed for digestion of biological materials. In order to evacuate the oven's interior of corrosive fumes, a one-quarter horsepower vacuum cleaner motor was attached to the already present louvers at the rear of the oven.

The general procedure for organic samples (NBS orchard leaves, bovine liver, fish and urine) was to heat the sample after the addition of 10-25 ml of concentrated nitric acid (Baker Ultrex) for 1.5 to 4 minutes in the micro-wave oven. The flask containing the solution was removed and cooled. To the solution was added 10-15 ml of 30% H_2O_2 and the solution was heated for 1-3 minutes with the microwave oven on defrost. If necessary the H_2O_2 treatment was repeated. The sample was then filtered (Gelman GA-6 0.5 micron filter) into a volumetric flask, using a vacuum device of our own design, and diluted with 1% nitric acid, which at present appears to be the best preservative and should be used with all samples when collected.

III. Results and Discussion

A. Optimum Conditions for Some of the Elements Investigated
Throughout this section, the modified detector was generally employed

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with the wire loop atomizer. Campbell and Ottaway[126] have suggested that standard solutions be prepared from oxy-anion salts, or metals dissolved in nitric acid, which reduces the degree of molecular vaporization for non-flame atomizers. This suggestion has been followed whenever possible. Linear portions of calibration plots have been evaluated by linear least square regression analysis.

1. Zinc: For zinc analysis all apparatus used to store or transfer solutions should be meticulously clean to avoid spurious analytical results. Although zinc has been detected in the disposable tips used for autopipettes, this problem was not evident from the atomic absorption method utilized here. However, the 10-ml disposable beakers supplied by Calbiochem and used as sample containers do have zinc as a trace impurity. Since these beakers cannot withstand acid pretreatment, 5-ml polypropylene beakers were used and are recommended instead. These beakers can withstand repeated acid washes to reduce the zinc contamination to below detectable levels. The optimum conditions are listed in table 4.

2. Manganese: Analysis of manganese in aqueous solutions is straight-forward. Both nitrate and chloride salts have been used with essentially identical results. Contamination poses no problem with any of the pipette tips or disposable beakers (conditions are listed in table 5).

3. Iron: The tungsten-rhenium wire loop has been shown to absorb radiation at 248.3 nanometers from an iron hollow cathode when the loop is heated without any sample on the wire. Upon prolonged heating at a given atomization temperature, the absorbance gradually decreases. Heating the loop at and above the normal atomization temperatures for a time gradually establishes a stable baseline near 0.00-0.01 absorbance units. With the assistance of x-ray fluorescence spectrometry, the presence of iron in the tungsten-rhenium alloy

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Table 4

Optimum Conditions for Zinc Analysis

Resonance Line: 213.9nm

Background Corrector Employed

Solution Conditions: Zn^o metal dissolved in conc. HNO_3

Standards prepared by serial

dilution and pH adjusted to

1.5-2.0

Storage Containers: Linear polyethylene

Brass Enclosure Atomizer

Flow Rates (Liters/minute): H_2 = 0.225 N_2 = 1.95 or Ar = 1.6

Atomization Temperature: 1430^oC

Step Mode

Slope of Calibration Curve: $1.98 \times 10^{-2} \pm 4.01 \times 10^{-4} \Delta A/ppb$

(Least Squares Fit)

Linear Range: 0-150ppb

Table 5

Optimum Conditions for Manganese

Resonance Line: 279.5nm

Background Corrector Employed

Solution Conditions: $Mn(NO_3)_2 \cdot 4H_2O$ dissolved in doubly

distilled deionized water and pH adjusted

to 1.5-2.0

Storage Containers: Borosilicate glass or linear polyethylene

Brass Enclosure Atomizer

Flow Rates (Liters/minute): H_2 = 0.225 N_2 = 1.95

Atomization Temperatures: $1630^{\circ}C$

Linear Voltage Program

Ramp Rate = 5.5

Slope of Calibration Curve: $1.69 \times 10^{-3} \pm 9.08 \times 10^{-5} \Delta A/ppb$

Linear Range: 0.650 ppb

was qualitatively yet unequivocally established. Even when a substantial amount of iron is not removed by heating, the analytical signal may be separated by use of high recorder speeds, so that the analytical sample signal precedes the iron signal. The conditions and analytical calibration curve data are shown in Table 6.

4. Chromium: Several reports have recently appeared in the literature indicating the significance of the valence state of chromium in the determination of chromium by flame atomic absorption spectroscopy. Green[127] suggests the use of hydrogen peroxide to convert all chromium to the chromium (III) state which may be determined with a greater sensitivity than the chromium oxidation state. Cresser and Hargett[128] noted the significance of pH control in analyzing solutions containing chromium VI. A nitrous oxide acetylene flame appeared to minimize the variation in the observed signal as the pH was varied between 3 and 9. Unfortunately, little has appeared to date in the literature regarding the significance of oxidation states when determining metals and non-metals by flameless atomic absorption. In work with a quartz-tube furnace, Vijan and Wood have shown selenium (VI) to give absorbance signals approximately 66% lower than the corresponding selenium (IV) signals.[129] Thus, it was of interest to investigate the effect of oxidation states of chromium on the absorbance signals observed when the tungsten-rhenium wire loop atomizer is employed. No difference in sensitivity was observed with change in oxidation state; in fact, optimum conditions are the same, as shown in Table 7.

5. Tin: Tin analysis is straightforward. Table 8 is indicative of the necessary conditions and of the calibration curves obtained.

6. Barium: The resonance line of barium is well into the visible region at 553.6 nm. A severe interference is observed from wire loop emissions. In order to make use of the wire loop technique for barium, these emissions must be masked. The hollow cathode image on the entrance slit to the monochromator

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Table 6

Optimum Conditions for Iron

Resonance Line: 248.3nm

Background Corrector Employed

Solution Conditions: Fe^O dissolved in conc. HNO_3 as stock

standard; working standards prepared by

serial dilution and pH adjusted to 1.5-2.0

Storage Containers: Linear polyethylene

Brass Enclosure Atomizer

Flow Rates (liters/minute): H_2 = 0.225 N_2 = 1.95

Atomization Temperature - 1745°C

Linear Voltage Program

Ramp Rate = 5.5

Slope of Calibration Curve: $6.06 \times 10^{-3} \pm 1.27 \times 10^{-4} \Delta A/ppb$

Linear Range: 0-400 ppb

Table 7

Optimum Conditions for Chromium

Resonance Line: 357.9nm

Background Corrector Employed

Solution Conditions: $CrCl_3$ dissolved in doubly distilled

deionized water and pH adjusted to

1.5-2.0; or $K_2Cr_2O_7$ dissolved in

doubly distilled deionized water.

Storage Containers: Linear polyethylene or borosilicate glass

Brass Enclosure Atomizer

Flow Rates (liters/minute): H_2 = 0.225 N_2 = 1.95

Atomization Temperature = 1795^oC

Step Mode

Slope of Calibration Curve: $5.59 \times 10^{-3} \pm 3.40 \times 10^{-5} \Delta A$/ppb.

Linear Range: 0-400 ppb

Table 8

Optimum Conditions for Tin

Resonance Line: 224.6 nm

Background Corrector Employed (Lamp current 10-20 ma necessary)

Solution Conditions: Sn^0 dissolved in 50 ml. of conc.

hydrochloric acid diluted to 250 ml used

as a stock standard; working standards

prepared by serial dilution with 1.5%

(v/v) nitric acid.

Storage Containers: Borosilicate glass

Brass Enclosure Atomizer

Flow Rates (liters/minute): H_2 = 0.225 N_2 = 1.7

Atomization Temperature: $1570^o C$

Step Mode

Slope of Calibration Curve: $4.0 \times 10^{-4} \pm 6.3 \times 10^{-6} \Delta A/ppb$

Linear Range: 0-230 ppb (for carbon rod, 0-270 ppb)

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is much smaller than the slit. By placing a piece of opaque tape with a hole 3 mm x 3 mm over the entrance slit, centered on the hollow cathode image, these emissions are removed.

Since the resonance line is in the visible region, hydrogen background correction could not be employed. A nearby neon line, 540.0 nm, emitted by the neon filler gas of the barium lamp, was utilized to correct for non-atomic absorption. Typical conditions are shown in table 9.

7. Selenium: Selenium is a very volatile element. Often during the drying stage, loss of selenium occurs. Several matrix modifications have been developed to reduce this loss during the drying stage. Furthermore, atomization rates may be reduced by formation of a less volatile species. Henn[130] described the use of molybdenum to reduce the losses. Attempts to employ this method have been unsuccessful. Ediga[131] initially demonstrated that nickel, added as the nitrate, reacts with selenium to form the less volatile compounds nickel selenate and nickel selenide. With the wire loop atomizer, addition of a 6 ppm Ni $(NO_3)_2$ matrix is suitable to reduce losses during the drying stage and to increase the sensitivity. The formation of reduced nickel-selenium compounds is possible if one considers that hydrogen gas may act as a reducing agent in the chemical reactions.

The typical conditions are shown in table 10.

8. Arsenic: Arsenic is similar to selenium in that it is a highly volatile element. In this laboratory it has been determined that the addition of lead salts greatly enhances the sensitivity of the method. This can be best explained on the basis that lead is less volatile than arsenic and therefore reduces the rate of atomization. However, lead is not sufficiently nonvolatile to cause signal suppression. Other metal salts, of a different volatility than lead, suppressed the signals. Standard conditions are listed in table 11.

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Table 9

Optimum Conditions for Barium

Resonance Line 553.5 nm

Background Corrector Not Employed. Background Correction Accomplished
   With a Nearby Neon Line (540.0 nm)

Solution Conditions: $Ba(NO_3)_2$ dissolved in doubly distilled
                      deionized water and pH adjusted to 1.5-2.0

Storage Containers: Linear polyethylene

Brass Enclosure Atomizer

Flow Rates (liters/minute): H_2 = 1.0   Ar = 1.6

Atomization Temperature: $1720^{\circ}C$

Step Mode

Slope of Calibration Curve: 2.5×10^{-3} $\pm 6.8 \times 10^{-5} \Delta A/ppb$

Linear Range: 0-220 ppb

Table 10

Optimum Conditions for Selenium

Resonance Line: 196.0 nm

Background Corrector Employed

Solution Conditions: Linear polyethylene

Absorption Cell Atomizer

Flow Rates (liters/minute) H_2 = 0.16 N_2 or Ar = 1.0

Atomization Temperature: 1570°C

Step Mode

Slope of Calibration Curve: 1.62×10^{-3} $\pm 4.3 \times 10^{-5} \Delta A/ppb$

Linear Range: 0-220 ppb

Table 11

Optimum Conditions for Arsenic

Resonance Line: 193.7 nm

Background Corrector Employed:

Solution Conditions: 0.1315 grams As_2O_3 dissolved in a minimum
of 0.1M NaOH, addition of 50 ml conc. HNO_3,
diluted with 0.1 M NaOH to 500 ml for stock
standard; working standards prepared by serial
dilution in 10^{-3}M $Pb(NO_3)_2$

Solution Containers: Linear polyethylene

Absorption Cell Atomizer

Flow Rates (liters/minute): H_2 = 0.16   Ar = 1.0

Atomization Temperature: 1520^oC

Step Mode

Slope of Calibration Curve: 1.37×10^{-3} $\pm$ $2.16 \times 10^{-5} \Delta A/ppm$

Linear Range: 0-180 ppb

9. Copper: Some difficulty was found in maintaining copper solutions at first, but the use of a polypropylene bottle solved the problem. Conditions are given in Table 12.

10. Cadmium: The optimum conditions for cadmium are given in Table 13. Matrix effects do not appear to be serious, but cadmium has an unusually small linear range that might be corrected by a special matrix.

11. Lead: Lead was analyzed successfully (Table 14), although it seems particularly subject to interferences when the wire loop is employed, but less so with the carbon rod.

B. Sensitivities

The absolute sensitivities (0.0044A) for the various elements and atomizers are listed in Table 15. The slope of a number of calibration plots for the wire loop and the carbon atomizers are shown in Table 16. In general the wire loop sensitivities are not quite as good as the carbon rod but they are quite close, and well below EPA standards for allowed concentrations in drinking water, as will be mentioned later.

The slopes of Table 16 approach the question of sensitivity from a different point of view. They do not correspond to the absolute sensitivities but are useful primarily for comparing other methods (i.e., spectrophotometry) to flameless absorption techniques.

C. Interference Effects

Several interference studies have been reported using the wire loop atomizer. It has been noted that the use of hydrogen gas greatly reduces the interference effects. Throughout this work, hydrogen was employed during the atomization process. Therefore, any discussion about interferences will not include the usefulness of hydrogen, but rather try to explain other interference affects on an atomic signal when hydrogen is employed.

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Table 12

Optimum Conditions for Copper

Resonance Line: 193.7 nm

Background Corrector (P & E 306 used)

Solution Containers: Linear polypropylene

Brass Enclosure Atomizer

Flow Rates (liters/minutes) H_2 = 0.15   A = 1.5

Atomization Temperature: $1150^{\circ}C$

Linear Range: 0-250 ppb

Table 13

Optimum Conditions for Cadmium

Resonance Line: 228.8 nm

Background Correct Not Used

Brass Enclosure Atomizer

Flow Rates (liters/minute) H_2 = 0.2 N_2 = 2.4

Atomization Temperature: $1740^{\circ}C$

Linear Range: 0-50 ppb.

Table 14

Optimum Conditions for Lead

Resonance Line: 217.0 nm

Background Corrector Not Used

Brass Enclosure Atomizer

Ramp Mode

Flow rates (liters/minute) H_2 = 0.23   N = 2.0

Atomization Temperature: 1000°C (Maybe too low)

Linear Range: 0-200 ppb.   (Maybe greater)

Table 15

Comparison of Absolute Sensitivities (in grams) for Non-flame Atomic Absorption Methods.

Element	Tungsten-Rhenium Wire Loop	Tantalum Ribbon[a]	Varian-Techtron[b] CRA 63	Instrumentation Lab[c] IL555CTF
Ba	1.2×10^{-11}	4×10^{-11}	7.2×10^{-12}	4.0×10^{-12}
Cr	5.6×10^{-12}	4×10^{-11}	6.4×10^{-12}	5.0×10^{-13}
Fe	3.2×10^{-12}	2×10^{-10}	2.0×10^{-12}	3.0×10^{-13}
Mn	9.4×10^{-12}	2×10^{-11}	1.5×10^{-12}	4.0×10^{-13}
Sn	5.2×10^{-11}	4×10^{-10}		6.0×10^{-13}
Zn	2.3×10^{-12}	4×10^{-12}	1.4×10^{-13}	—
As	1.4×10^{-11}	6×10^{-10}	—	—
Se	1.8×10^{-11}	7×10^{-10}	3.9×10^{-12}	—
Cd	4.5×10^{-12}	7×10^{-12}	—	—
Cu	4.5×10^{-11}	2×10^{-11}	3.5×10^{-12}	—
Pb	2.7×10^{-11}	3×10^{-11}	—	—

(a) Reference 17

(b) Determined in this study

(c) Instrumentation Laboratory, Inc. Brochure.

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Table 16

Comparison of Sensitivities (Calibration Plot Slope)

for the Wire Loop and Varian-Techtron CRA 63 Atomizers

	Slope (ΔAbs./Δppb)	
Element	Wire Loop	CRA 63
As	1.3×10^{-3}	———
Ba	2.5×10^{-3}	2.5×10^{-3}
Cr	5.6×10^{-3}	3.6×10^{-3}
Fe	6.0×10^{-3}	6.7×10^{-3}
Mn	1.7×10^{-3}	1.3×10^{-2}
Se	1.6×10^{-3}	5.6×10^{-3}
Sn	4.0×10^{-4}	———
Zn	1.99×10^{-2}	9.1×10^{-2}

For most of the elements examined, some limited study was made of the change in peak absorbance signal in the presence and absence of possible interferents such as the sodium salts of various anions and several transition metal salts, Table 17. Most of the interference evaluations were carried out at a single analyte and interferent concentration, the latter being much larger than would usually be found in water samples. Optimum conditions were used throughout the experiments. Any interferent causing a 10 percent charge in signal was considered to be significant. Smeyers-Verbeke et al[132] have shown that the sign of the interference may change with interferent concentrations. Thus, variation of the interference concentration as well as the analyte-to-interferent concentration ratio is necessary for a complete evaluation of interferences for a given element.[133] Furthermore, the effect of multiple interferents on a signal has also been investigated and is shown in Table 18.

First, referring to Table 17, iron as the chloride caused a rather severe depression in the zinc and chromium peak absorbance signals. Since iron salts have relatively low volatility compared to zinc and chromium salts, the interference may have occurred on the wire by preventing effective volatilization of the analyte. Interestingly enough, cupric sulfate at 1-millimolar levels enhances the zinc signal, but suppresses the chromium and manganese signals. The rate of evaporation of zinc or the zinc salts from the loop was probably reduced in the presence of cupric sulfate, allowing the detection system to follow the peak absorbance signal more efficiently for the volatile element. The results for chromium and manganese with a less volatile copper interferent are difficult to explain.

Yet it is interesting to note that Sensmeir et al[134] found a similar depression for manganese when employing a tantalum strip atomizer. Further,

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Table 17

Evaluation of Interferents for Analysis with the Wire Loop Atomizer,
% Change in Absorbance

Interferent, 10^{-3} M Salt		Cr^b 1.0ppm	Zn 1.0ppm	Mn^b 0.1ppm	Mn^d 0.1ppm	Se 0.1ppm	Se^d 0.1ppm	Ba 0.1ppm	Ba^d 0.1ppm
Fe	$FeCl_3$ (HCl matrix)	-59	-30^a	-15	0	-13	-9	-13	-6
	$Fe(NO_3)_3 \cdot 9H_2O$	---	---	-12	0	+1	+8	+5	+1
Cu	$CuSO_4 \cdot 5H_2O$	-19	+31	$-54,^c -32$	+6	-25	-37	-31	-45
Mn	$MnSO_4 \cdot H_2O$	0	+15	---	---	-37	-51	-16	-9
	$MnCl_2 \cdot 4H_2O$	---	---	---	---	-17	-20	---	---
Cd	$3CdSO_4 \cdot 8H_2O$	0	+12	$-19^c, -2$	-2	-26	-24	-17	-40
	$CdCl_2 \cdot 2\frac{1}{2}H_2O$	---	---	-7	-7	-12	-19	---	---
Pb	$Pb(NO_3)_2$	0	---	+2	+5	-100	-88	-10	-15
Zn	$Zn(NO_3)_2 \cdot HNO_3$ matrix)	0	---	+4	-1	+3	-25	---	---
Ca	$Ca(NO_3)_2 \cdot 4H_2O$	---	---	-6	+13	-40	-41	---	---
NO_3^-	$NaNO_3$	-11	-28	-16^c	---	---	---	---	---
Cl^-	$NaCl$	0	-32	$-1,^c +7$	-10	-3	-20	+18	+50
SO_4^-	Na_2SO_4	-13	-16	-30^c	---	---	---	-30	-70
PO_4^{-3}	$Na_3PO_4 \cdot 12H_2O$	---	---	-12	+2	-22	-3	---	---
F^-	NaF	---	---	-29	-1	-24	-16	---	---
I^-	NaI	---	---	---	---	---	---	---	---
CO_3^{-2}	$Na_2CO_3 \cdot 4H_2O$	0	-23	---	---	---	---	---	---
Br^-	$NaBr$	0	-40	+16	+21	-2	-8	-2	+31
Mg	$MgCl_2 \cdot 6H_2O$	---	---	-19	+5	+7	-20	---	---
CO_3^{-2}	$NaHCO_3$	---	-19	---	---	---	---	---	---
CN^-	$NaCN$	---	---	+6	-12	-14	-21	---	---

a) 2.2ppm   b) LVP employed   c) 0.2ppm   d) CRA63 analysis

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difficulty is encountered in trying to explain the results for manganese when sodium bromide and sodium fluoride are present. Iron suppressed the manganese signal. Iron, being less volatile than manganese, probably interfered with the atomization of manganese. It is also possible that, as with magnesium chloride hexahydrate, the formation of chloride salts gives rise to losses due to molecular vaporization. Similar results have been obtained by West et al[134a] and by Kinoshita[135], who employed carbon-filament and carbon-tube atomizers, respectively.

Interferences for selenium all show a trend of depression of the analyte signal. In the case of lead, the depression can simply be explained as the formation of the insoluble selenate. Barium interferences are generally a suppression of the atomic signal. For all the sulfate salts, the precipitation of barium sulfate would lead to a decrease in atomic signal. Since the extent of decrease in signal changes obtained differs with each of the salts, a combined cation-anion suppression effect must be occuring.

From Table 17, the interference effects on the carbon rod atomizer may be compared to the values obtained for the loop atomizer. In general, there is no strict pattern of interference. One general conclusion may be drawn. The wire loop, although prone to artificial interferences, as is the carbon rod atomizer, shows less suppression or enhancement as compared to the carbon rod.

Referring to Table 18, one will observe that when solutions containing each of the interferents were analyzed, signal depressions or enhancements could not be predicted from the results previously shown in Table 17. Seusmeier et al[134], as well as Maruta and Takeuchi,[20] commented on the complex pattern generally observed for interferences in the lack of coherent theory to explain their origin.

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Table 18

Multiple Interference Effects

Element	Interferents, 10^{-3}M	% Signal Change
Mn[a]	Cu^{+2}, Cd^{+2}, NO_3^-, Cl^-, SO_4^{-2}	-40
Zn[b]	Fe^{+2}, Cu^{+2}, Mn^{+2}, Pb^{+2}, NO_3^-, SO_4^{-2}	-20
Ba[b]	Pb^{+2}, SO_4^{-2}, Cd^{+2}, CO_3^{-2}	-82
Se[b]	Fe^{+2}, Pb^{+2}, Mn^{+2}, PO_4^{-3}, Zn^{+2}, Ca^{+2}	-15

a) 0.2 ppm

b) 0.1 ppm

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Obviously, the most important inference to be made from this inter-ference study is that since a multitude of interferences exists when the aliquot method is employed, the use of calibration curves for the deter-mination of unknown concentrations must be viewed with caution. With the existence of a linear working curve for a particular element, both the method of standard additions and a calibration curve should be carried out for any matrix suspected of enhancing or suppressing the analyte signal. If the standard additions plot and the calibration curve parallel one another, then no observable matrix effect exists.

Another type of interference observed in this study was that of wire loop emissions giving rise to incandescent noise. Stray light striking the detector has been both experimentally and theoretically shown to create non-linear calibration curves. This generally occurs only when a continuum source and unmodulated circuitry is employed. However, during the analysis of barium, whose resonance line is located in the visible region, incadescent noise was observed. Initially the atomic signal and then the incandescent noise were seen at the end of the atomization period. This noise saturated the photo-multiplier tube and gave rise to very poor precision.

Similar results have been obtained with the carbon-rod atomizer. In order to minimize the effect, it is necessary to keep the ac to dc signal ratio as high as possible. Varian supplies an accessory to reduce the effect, yet a simple piece of masking tape with a hole 3 mm by 3 mm placed on the face of the entrance slit removed this effect completely with no loss in sensitivity and with improved precision.

It is well known that elements with low ionization potentials have a tendency to ionize rather than atomize, reducing the sensitivity of analysis in conventional flame spectroscopy.[136] Ottoway and Shaw[137] have shown that

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ionization is about 40 times less in carbon furnace techniques than with conventional flame techniques. Addition of an alkali metal salt did not enhance the sensitivity; however, it did decrease the amount of ionization.

It was of interest to determine whether ionization interference is significant when the wire loop atomizer is utilized. In order to estimate the extent of atomization and ionization, the atomic resonance line 553.6 nm and the most intense ion line, 455.4 nm were monitored. The extent of ionization of the extremely high concentration of 20 ppm Ba is virtually zero and the absorbance can be considered an atomic signal. This phenomenon may be attributed to the low optimum temperature required during wire loop analysis.

There are several troublesome interferences which can only be diagnosed and removed by visual inspection. During the drying cycle it is necessary to visually verify that the sample evaporate smoothly and identically each time. When the drying temperature is too high, the drying is erratic and generally causes losses by splattering. When one wishes to arrive at the optimum atomization temperature for any given matrix, maximum signal peak absorbance is important, yet equally important is the precision. Therefore, oftentimes the maximum absorbance was not obtained, but rather a reproducible signal with a slight concomitant loss in absorbance.

A special study was made of some interferences in the analysis of lead. The idea was to see the effects of a complexing agent (EDTA) and different pH levels on the suppression of the lead signal of phosphate, carbonate, sulfate and iodide. Since these anions form insoluble precipitates with lead, it was hoped that pH control and/or the addition of EDTA would be beneficial. It was found the EDTA itself depressed the signal. However at low pH's

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there was less depression of the lead signal by carbonate and sulfate
(~ -25% - other typical values were about -50%). One can conclude that
the EDTA is not of much help. Other methods must be used for the removal
of interferences. Nevertheless, solutions containing 1% HNO_3 were con-
sistently freer from interferences. Thus the standard procedure of making
samples acidic with HNO_3 still appears to be the best approach.

D. Applications

1. Water Analysis: The aliquot method using linear voltage pro-
gramming (LVP) was applied to three sets of EPA Quality Control Samples
supplied by the Environmental Monitoring and Support Laboratories, Cincinnati,
Ohio. All samples after dilution contained 0.15% nitric acid. Dilutions
were such that the absorbance fell on the linear portion of the calibration
curves and then the appropriate multiplying factor applied. The results
are shown in Table 19. It can be seen that the relative standard deviations
are in general better than 5%. At least five runs were made on each sample.
All of these values were taken from calibration plots rather than by standard
additions or other techniques. The accuracy varied to a degree, but the
variation seemed random except in the case of zinc. Since it is unusual to
find low zinc results because zinc is a wide spread contaminant, the true
values may be suspect. Little or no matrix effects could be expected for
the diluted EPA samples, although some such effect might exist since the
most concentrated sample (No. 3) contains about 3500 ppb of total metals.

Finished water samples provided by the U.S. Army, which had been analyzed
by the carbon rod or flame methods, were analyzed by the wire loop atomizer,
Table 20.

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Table 19

Results of EPA Sample Analysis with Relative Standard Deviations

Results in ppb

Sample Number

Metal	1		2		3	
	True Value	Found	True Value	Found	True Value	Found
Zn	11	$9 \pm 0\%$	30	$20 \pm 2.2\%$	174	$160 \pm 1.5\%$
Fe	26	$24 \pm 2.6\%$	417	$420 \pm 0\%$	678	$653 \pm 2.5\%$
Cr	16	$16 \pm 5.4\%$	154	$148 \pm 1.1\%$	209	$185 \pm 3.9\%$
Pb	22	$12 \pm 10\%$	298	$293 \pm 6.2\%$	352	$338 \pm 1.9\%$
Mn	26	$31 \pm 0.9\%$	45	$48 \pm 1.1\%$	397	$390 \pm 4.6\%$
Cd	5.2	$4.5 \pm 4.6\%$	23	$24 \pm 4.6\%$	73	$68 \pm 4.8\%$
Cu	16	$16 \pm 1.9\%$	72	$64 \pm 2.7\%$	102	$73 \pm 0.9\%$
Se	---	-----	26	$32 \pm 1.7\%$	44	$41 \pm 3.5\%$
As	26	$23 \pm 1.4\%$	109	$107 \pm 1.9\%$	154	$146 \pm 2.7\%$

Table 20

Results for Drinking Waters and Water Effluent
Samples of Unknown Contents

Sample Code	Element	Wire Loop (ppb)	Carbon Rod (ppb)
60	Cd	13[b]	15
79		14[b]	14
92	Cu	123[b]	124
94		178[b]	198
60	Ag	28	28[a], 29
65		24	31[a], 31
79		25	30[a], 30
19		24	31, 32[a]
60	Zn	174	141[a] 196[c]
65		173	136[a] 184[c]
79		169	183[a] 196[c]
75		157	202[a] 216[c]
10		14	28[a]
58	Mn	132	132 181[a]
78		15	28
59		20	30[a] 22
65		11	20
10		1835	750[a] 1820
90	Fe	900, 1800[b]	2051[a] 2200[c]
58		49.5	285[a]
59		1800, 3900[b]	3925[a] 4900[c]

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Table 20

(continued)

Sample Code	Element	Wire Loop (ppb)	Carbon Rod (ppb)
60	Pb	37	19[a]
65		18	19[a]
59		11	8[a]
79		26	19[a]
75		14	6[a]
19		7	19[a]
60	Cr	18	38
65		17	23[a], 35
79		18	35
19		16	39
58	Ba	5	11
65		11	26
79		18	19
10		30	42

a) Results from Army Laboratory

b) Standard Additions used

c) Flame AAS - from this laboratory

The zinc concentrations, determined by the aliquot method, were neither consistently lower or higher than those found by the Army laboratory. In the case of four water samples having zinc concentrations between 100 and 200 ppb, two of these samples, analyzed by the aliquot method, gave values intermediate between those obtained with flame atomic absorption and carbon rod analysis. Zinc was the only element examined to give a non-zero absorbance for a blank consisting of doubly-distilled deionized water. The remaining two samples were found to have zinc concentrations slightly lower than those predicted by the other two atomic absorption techniques. Because of curvature of zinc calibration curves, it was not possible to check for matrix effects by the method of standard additions.

Severe matrix effects were observed for the iron analysis. The concentrations of iron found in samples 58, 59, and 90 by the aliquot method were much lower than expected. Our preliminary results, obtained with the carbon rod atomizer, were in agreement with the other values. For samples 90 and 59, the iron concentrations were determined by flame atomic absorption analysis of the undiluted samples and by the aliquot method employing both calibration curves and the method of standard additions. By these methods, the concentrations obtained were in good agreement with the Army laboratory results. However, the results derived from the working curves were approximately one-half of those found by standard additions. The reason for signal suppression by the matrix is not known, but has been circumvented by the standard additions method.

Wherever the independent manganese analyses were not in agreement with the aliquot method determinations, analyses in our laboratory, employing the

carbon rod atomizer, corroborated the results from the latter method. For samples 78 and 65, the lower manganese concentrations obtained with aliquot sampling relative to the carbon rod atomizer indicated a possible matrix signal suppression.

There was good agreement between the wire loop and carbon rod analyses for barium. Unfortunately, the concentrations were below the limits of detection for the flame analyses performed by the Army laboratories. From the results obtained in our laboratory, there is little concern about any matrix interferences in these analyses.

2. <u>Microwave Oven Digestion Procedures and Analysis of Biological Materials.</u>

Several methods of biological digestion of trace metal analysis have been described in the literature. Most of these procedures require low temperatures, refluxing with strong oxidizing agents, and long periods of time for complete digestion. Initial experiments began in our laboratory with azalea stems and leaves. A series of plant stems were placed in 50 ppm selenium solutions for 3 days, while other stems simply fed on tap water. Samples that were soaking in selenium solutions turned red indicating some selenium uptake was occurring. The samples were dried for 24 hours at 90°C and then ground in a mortar and pestle. One gram samples required 8-10 hours of reflux for complete digestion in 50/50 mixtures of 68% HNO_3- 70% $HClO_4$ and 68% HNO_3- 30% H_2O_2. Since, one of the features of wire loop analysis is the speed of analyses, a more efficient means of digestion was desirable to enhance the overall efficiency of the wire loop method. Kroityohann <u>et al</u>[137] reported the use of a microwave oven digestion technique employing a nitric acid-perchloric acid digestion medium. It was recognized in our laboratory from the analysis of the azalea samples which had been digested with a nitric acid-perchloric acid medium, that perchloric acid attached to the

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wire loop surface. Therefore, if the microwave oven technique was to be useful, an oxidizing agent other than perchloric acid would be required. Several acid mixtures were attempted. The best medium for complete digestion, with little explosion hazard, was 68% HNO_3- 30% H_2O_2 (for digestion of NBS standard samples, as discussed in the Experimental Section.) A more severe background was seen when the perchloric acid was employed. Furthermore, D. C. Manning et al[138] have shown that a nitric acid-hydrogen peroxide digestion is preferred to avoid chloride interference. The digestion procedure was used to analyze NBS samples and the results are shown on Table 21. All samples and standards underwent the same digestion and digested standards were checked against undigested standards to check for volatility losses. No losses due to volatility were found.

Fish samples were digested by the microwave oven technique. Nearly complete digestion was obtained. Analyses were carried out for manganese and iron by both the aliquot method and the carbon rod method. The results are shown in Table 22. In general the relative standard deviations are about equal for both methods. Yet, the wire loop analysis requires less overall analysis time. It was necessary to use the method of standard additions. This was primarily due to the fatty acids which have usually been difficult to completely digest.

Several methods for the analysis of manganese and chromium in urine have been developed. These include spectrophotometric,[139] colorimetric,[140] neutron activation,[141] gas chromatographic,[142] and atomic absorption techniques for chromium and colorimetric,[143] neutron activation and atomic absorption[144-146] methods for manganese.

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Table 21

Analysis of NBS Organic Samples

SRM 1571 Orchard Leaves

Sample No.	Sample Size (grams)	Mn found (mg/g)	% Error	As found (mg/g)	% Error	Zn found (mg/g)	% Error
1	0.159	86.8	4.1	----	----	----	----
2	0.1028	86.5	4.8	----	----	----	----
3	0.0571	89.3	1.9	----	----	----	----
4	0.1108	98.3	8.1	----	----	----	----
5	0.1216	93.7	3.1	----	----	----	----
6	0.0807	95.4	5.5	----	----	----	----
7	0.1037	86.8	4.2	----	----	----	----
8	0.5035	----	----	13.7	2.14	28.2	12.8
9	0.4625	----	----	13.5	3.57	25.7	2.8
10	0.4876	----	----	14.3	2.14	24.2	3.2
NBS Certified Values (mg/g)		$91.\pm4$		14 ± 2		25 ± 3	

SRM 1577 Bovine Liver

Sample No.	Sample Size (grams)	Mn found (mg/g)	% Error	Se found (mg/g)	% Error	Zn found (mg/g)	% Error
1	0.5186	10.4	0.97	1.04	5.45	125	3.84
2	0.5276	11.8	14.6	0.97	11.8	133	2.31
3	0.2756	10.7	3.9	0.99	10.0	131	0.77
4	0.2501	9.5	7.8	1.09	0.91	129	0.77
NBS Certified Values (mg/g)		10.3 ± 1		1.1 ± 0.1		130 ± 10	

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Table 22

Analysis of Fish Samples

Sample No.	Specie	Sample Size, grams	Fe Wire Loop	Fe CRA	Mn Wire Loop	Mn CRA	Zn Wire Loop	Zn CRA
1	Mullet	2.0705	4.07 (2.5)*	3.95 (2.4)	0.17 (1.7)	0.16 (1.6)	14.8 (0.90)	15.3 (1.5)
2	Mullet	2.2527	4.20 (7.3)	4.12 (6.5)	0.20 (5.8)	0.25 (4.7)	14.1 (0.95)	15.6 (1.1)
3	Speckeled Trout	2.1764	2.57 (4.8)	2.40 (5.3)	0.35 (4.7)	0.32 (5.3)	10.4 (0.5)	10.5 (2.0)
4	Speckeled Trout	1.9817	2.43 (3.4)	2.54 (4.2)	0.31 (3.9)	0.27 (4.6)	8.7 (6.7)	10.7 (4.3)
5	Speckeled Trout	2.2403	2.51 (6.5)	2.62 (7.4)	0.32 (5.9)	0.35 (5.7)	9.3 (2.5)	8.5 (4.2)

*() values in parethesis are % relative standard derivations.

Usually the colorimetric analyses and spectrometric analyses for manganese are slow and lack reliability. Besides, the reported values for urine, manganese levels are about 1-10 ppb and the sensitivity requirements are usually met only with neutron activation or atomic absorption methods. The atomic absorption techniques require lengthy extraction procedures or sufficient time for digestion. Low concentrations of chromium (20 ppb) have required a preconcentration step and even its isolation from the matrix for analysis.

With the use of microwave oven digestion a fast, efficient and accurate anal sis for both chromium and manganese has been developed. Longer digestion times were required (such that the digests turned colorless and clear.) The results for urine samples are shown in Table 23.

3. Cr^{+3}/Cr^{+6} Separation and Analysis: A method has been developed to allow for rapid and sensitive separation and determination of the tri- and hexavalent states of chromium.

Several methods have been developed utilizing chelation-solvent extraction techniques for the determination of chromium in fresh waters[147] and in seawater.[148] Ion exchange chromatography together with atomic absorption spectroscopy has been employed for the determination of the two main oxidation states of chromium.[149] All of these methods require extensive preparatory lab work. In our laboratories, an enormous background signal was obtained when chelating agents, such as ammonium pyrollidine dithiocarbamate (APDC) were used to pre-concentrate chromium for wire loop analysis. Hence, chelating agents should be avoided. F. J. Feldman et al[150] were able to extract Cr(VI) simply with methylisobutyl ketone (MIBK). Biological samples were digested, an oxidizing agent added to the sample digest to assure that all the chromium was in the hexavalent oxidation state, and Cr(VI) was extracted into MIBK. Attempts to

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Table 23

Analysis of Urine

Sample no.	Aliquot no.	Sample volume ml	Concentration found, ppb			
			Mn		Cr	
I	1	15	6.0	(4.7)*	18.9	(1.8)
	2	15	5.7	(3.8)	19.7	(1.9)
	3	15	6.7	(2.9)	17.9	(2.1)
	4	15	6.5	(6.7)	18.4	(1.7)
II	5	15	8.2	(1.5)	21.7	(2.0)
	6	15	8.7	(2.4)	21.5	(2.5)
	7	15	9.4	(2.7)	20.9	(1.8)
	8	15	8.5	(3.9)	21.2	(3.9)
	9	15	8.0	(4.0)	21.8	(4.2)

* () values in parenthesis are % relative standard deviation

repeat the work in this laboratory were unsuccessful. Failure to repeat Feldman's work has been reported by several other workers.[151,152]

Work in this laboratory determined that the order in which the reagents were added to the sample governed the success of the extraction. The procedure followed in this laboratory is shown in Table 24. Katz et al[153] had investigated the mechanism by which chromium was extracted with MIBK and is supported by the work in this laboratory.

The method was evaluated by preparing mixed valence samples and proceeding with the extraction procedures. In all cases, the recoveries of chromium (VI) were better than 97 percent as seen by comparing signals of chromium (VI) aqueous standards. The aqueous phase was analyzed for Cr(III) and recoveries were better than 96%. We were not aware of any mixed valence biological standards and therefore chose to work with available samples by oxidizing any Cr(III) to Cr(VI) and proceeding with the extraction procedure.

4. Analysis of Organotin Compounds: Since organotin compounds are used extensively in marine paints as antifouling agents, a brief survey was run on a series of tributyl tin salts. A brief study was done and it was found that a relatively high atomization temperature ($1800^{o}C$) was needed for the loop, which is surprising since these compounds were expected to be quite volatile. Evidently decomposition to the oxide takes place easily. The organotin compounds were run, with xylene and MIBK as solvents, and the following results were obtained:

	Wire Loop	CRA
Sensitivity:	4.9×10^{-11} g	1.7×10^{-11} g
Linear Range:	0 - 260 ppb	0 - 330 ppb

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Table 24

Chromium Extraction Procedure

(1) An appropriate quantity of sample solution (5-10 ml) is placed into a
60 ml separatory funnel.

(2) To the separatory funnel is added an equal quantity of methylisobutyl
ketone and enough concentrated hydrochloric acid to obtain a 3N solution
in hydrogen ion.

(3) Shake the solution vigorously for 30 seconds, chill the solution and
allow the phases to separate.

(4) Analyze the aqueous layer for Chromium (III) and the organic layer for
Chromium (VI).

E. Conclusions

We have found that the wire loop atomizer of our design can be successfully used as an electrothermal atomizer. It compares well with carbon rod or cup atomizers. Although the wire is a bit less sensitive, it is much cheaper and easier to run than carbon atomizers. The wire, for some samples, is not as subject to matrix effects but these are still important and must be checked for each sample type. The method of standard additions has proved successful in a number of cases. Optimum conditions for zinc, iron, silver, chromium, manganese, barium, lead, copper, cadmium, selenium and arsenic have been determined. It has been found that the use of hydrogen (mixed with nitrogen or argon), even on the drying cycle, produces superior results. Since the signal is quite brief when the wire loop is used, reduction of the capacitance of the damping capacitors allows

quicker instrument response for the Varian AA5 atomic absorption spectrometer. (This may not be necessary for Perkin-Elmer instruments). Volatile elements (As and Se) are analyzed more accurately when a glass absorption cell with quartz windows is used. The detection limits vary with the element being analyzed, but are on the order of a few ppb with linear analytical ranges often in the region up to several hundred ppb.

Digestion methods have been developed to handle various organic samples. An extraction method for chromium (VI) has been perfected which allows the separation of chromium (III) from chromium (VI).

The standard deviations found have usually been below 5%, although the accuracy may not be as good in all cases. The analysis of EPA samples was quite successful in terms of accuracy, as were most of the Army water samples. Our detection limits are generally well below EPA standards (Table 26) except for Se, which we believe we can improve with the newest instrument modifications.

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Table 25

Comparison of Extraction and Direct Analysis

of Chromium from EPA Samples

#1		#2		#3	
True	Found	True	Found	True	Found
16	16 $\pm$ 5.4%	154	148 $\pm$ 1.1%	209	185 $\pm$ 3.0
16	* 17 $\pm$ 4.1%	154	* 146 $\pm$ 0.9%	209	* 201 $\pm$ 3.8%
16	* 15 $\pm$ 5.7%	154	* 149 $\pm$ 1.2%	209	* 206 $\pm$ 4.9%

* MIBK Extraction

Lyophilized Serum Samples

	#1	#2
Cr Found (mg/g)	0.547 $\pm$ 6.7%	0.541 $\pm$ 4.3%

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Table 26

Detection Limits with EPA Standards

Element	EPA, Interim Standard (ppb)*	Aliquot Method Detection Limit ppb
As	50	8
Ba	1000	7
Cr	50	3
Fe	--	2
Mn	--	2
Se	10	10
Sn	--	10
Zn	5000	1

*Environmental Protection Agency: Federal Register, 40, 59566 (1975); 42, 35764 (1977).

Future Work: Several things might be considered for future work. The apparatus might be improved in several ways. Now we feel we have optimized AA-5 as much as possible. However, a simple electronic peak height analyzer might be added to eliminate recorder lag. The absorption cell could be improved and used for all elements in an attempt to prevent any oxygen from coming in contact with the wire.

Whether the presence of small amounts of oxygen has an effect on the analysis of some elements is still in doubt. Some studies of the mechanism of atomization have been done but these are not complete enough to give us a good understanding. Further optimization of conditions might improve the accuracy of analysis of some elements. Since many matrix effects seem to be due to extraneous salts that prevent atomization of the analyte, it might be possible to decrease this effect by using a larger diameter wire which would increase atomization efficiency.

The mechanism of concentration of metals on the surface from aqueous solution should be studied further--first, to understand the effect and second, to possibly develop a field sampling technique that would be more efficient. Possibly some elements could be "fixed" on the wire by electro-lytic reduction (silver may well do this spontaneously). This opens not only the field of electrochemical studies of tungsten wires as electrodes but also the atomization of a metal as opposed to a salt since the two may be quite different.

Finally, some form of a wire loop atomizer might be adapted as a chromatographic detector for metal chelates.

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